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Electrical Discharge Flash Pyrolysis of Biomass

by

A.N. Sivell, J.M. Beeckmans and A.R. Webster

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by

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October 1983

TEARSHEET ANNOTATION

Ultrafast pyrolysis of biomaterials was demonstrated using an exploding wire technique. Hydrogen, carbon monoxide and light hydrocarbons were produced.

ABSTRACT

A study of electrical discharge flash pyrolysis of biomass has been completed at the University of Western Ontario. The experiments consisted of discharging a high voltage capacitor (320 joules) through biomass samples held between two electrodes.

Pellet samples made from graphite and cellulose were not pyrolysed by the discharge. The electrical energy could not be coupled to the sample to achieve any measureable pyrolysis. Conductive string samples showed similar results.

Discharge through a thin wire (6/1000 in) pyrolyzed the biomass layer on the surface of the wire. Gas analysis of the pyrolysis gases showed the mixture contained mainly hydrogen and carbon monoxide with low concentrations of carbon dioxide and hydrocarbons.

The effects of sample constitution (lignin, birch flour, and cellulose), sample mass, and initial water content and the composition of the gas surrounding the sample were determined.

It was discovered that the presence of a glass

containment tube, open at both ends, around the sample produced a very substaintial increase in yield of gases.

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1 INTRODUCTION

Gasification technology had been developed and followed a path of improvement up until the early 1930 's, when large amounts of natural gas became available. Since then gasification and pyrolysis have again come to the forefront of scientific research, due to the increasing cost of oil and eventual depletion of oil and gas reserves.

Pyrolysis is the thermal degradation of organic compounds in the absence of oxygen to produce smaller, lighter gas molecules. At temperatures above 200 degrees C lignocellulosic materials thermally degrade to produce gases, liquids (tar) and solids (char) as primary products. Depending on reaction parameters, temperature, pressure, heating rate, residence time, moisture content, ash content and the presence or absence of oxygen, the primary products can undergo secondary reactions affecting yields and qualities of the final products.

Flash pyrolysis involves very rapid heating of biomass in the absence of air, followed by rapid quenching of the reaction products. This process maximizes conversion of biomass feedstocks to gaseous products, and suggests the feasibility of a fast pyrolysis process supplying light hydrocarbons as feedstocks for further chemical synthesis.

Flash pyrolysis shows promise as a method for upgrading the quality of products obtainable from wood, compared to slower conventional pyrolysis methods.

This report focuses on the results of a study undertaken at the University of Western Ontario, on the fast pyrolysis of biomass using an electrical discharge as an energy source. It was initially intended to achieve almost instantaneous pyrolysis by discharging a large high voltage capacitor through the biomass contained between two electrodes. This approach was found not to be feasible, and an exploding wire technique was used instead to pyrolyse the biomass in very short times. A high voltage electrical discharge is capable of providing ionized gas molecules or very reactive free radicals during pyrolysis, which opens the possibility that an improved product distribution will result.

2 EQUIPMENT AND MATERIALS

2.1 Electrical Equipment

The circuit diagram, Figure 1, illustrates the main equipment components used for supplying electrical energy to the test cell. Power from the mains passed through a variable mains transformer into a high voltage power supply. The electricity was then converted to a high voltage, low current DC form. Two 12 Mohm resistors were connected in series with the power supply, limiting the current to below 1mA. The electrical energy was then stored in a 1.6 uF capacitor until discharged to ground through the test cell. A wire-wound inductor was designed and built. Inclusion of the inductor between the capcitor and test cell reduced the current and lengthened the duration of the discharge. The inductor was used for most of the testing on pellet and string samples. The equipment described above is listed in Table 1, along with some specifications and dimensions.

During the course of the experimental investigation three different methods were used to initiate the discharge of the capacitor through the test cell. In two of these methods high voltage switches were used, whereas in the third method discharge occurred when the potential between two electrodes was great enough to cause spontaneous

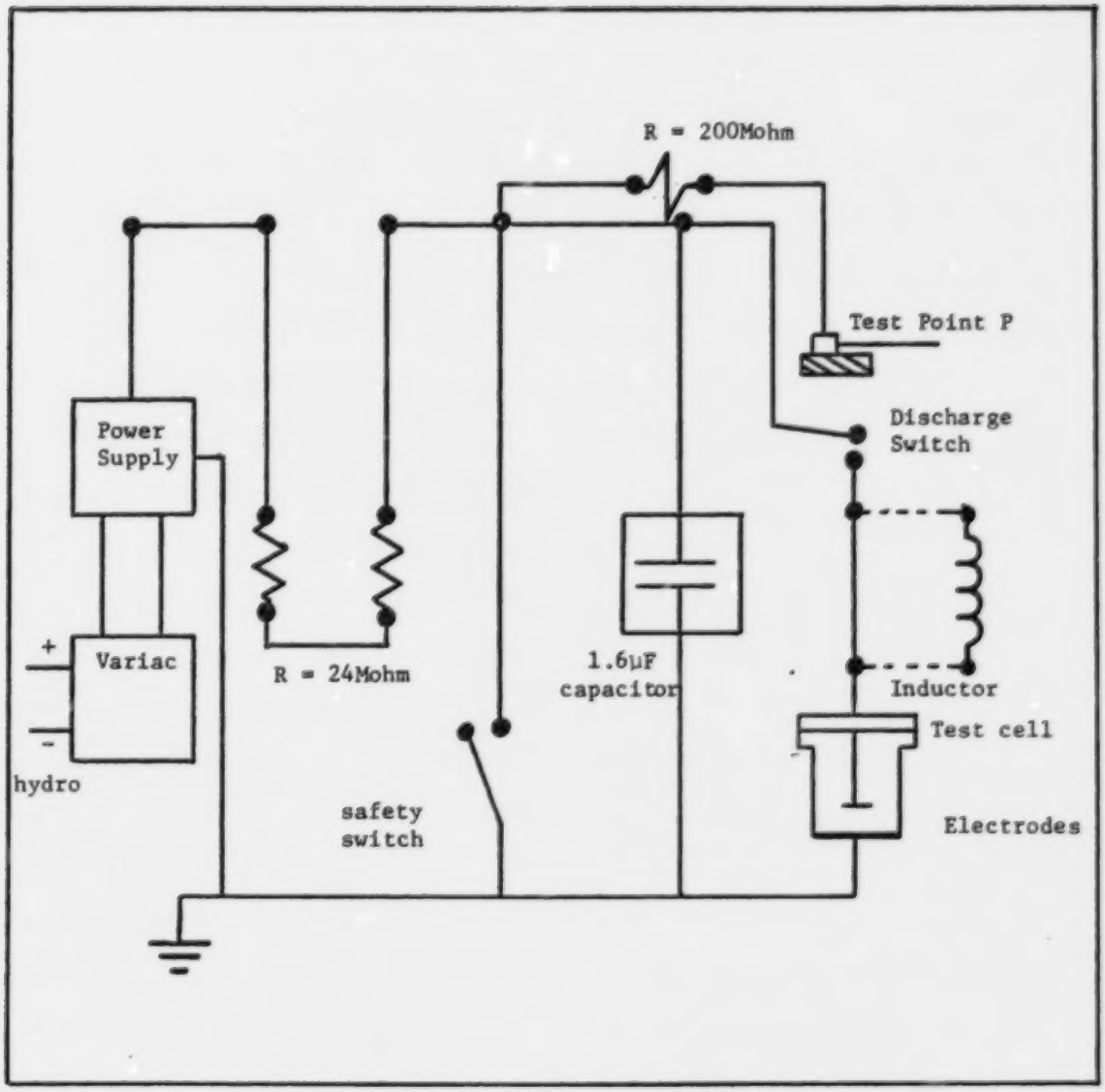

FIGURE 1: Circuit Diagram for Electrical Components

TABLE 1

Electrical Equipment Specifications
and Dimensions

Power Supply	physical dimensions: height 18 cm, length 13 cm, width 13 cm input capacity: 120 volts at 15 amperes output capacity: 20,000 volts DC at 1.25 m amperes
Capacitor	physical dimensions: height 36 cm, length 64 cm, width 18 cm capacity: 1.6 μF (320 Joules @ 20 kV) Type: Parallel plates isolated with oil.
Resistors	physical dimensions: length 18 cm, diameter 3 cm rating: 12 M ohms
Inductor	physical dimensions: diameter 16.5 cm, length 53 cm coils spacing 10/in inductance: 2.18 mh resistance: 35 ohm

breakdown.

One high voltage switch consisted of two brass contacts (diameter 6.4 mm) separated by a 0.1 to 2 cm air gap. The air gap was adjusted so that breakdown occurred at a specified voltage. At breakdown the electricity stored in the capacitor short-circuited to the second contact and then passed through the sample to ground. The second voltage switch was a vacuum relay rated for 50 KV and 600 amperes. This high voltage vacuum relay was actuated by a simple switch mechanism.

2.2 Safety Equipment

Several safety features were incorporated in the equipment design. A 0.76 m high, 1.2 m long, by .8 m wide expanded mesh metal box contained all the electrical equipment. This box was grounded to a cold water pipe with heavy braided wire. Half the front face of the box was a large door for access to the equipment and test apparatus. A micro switch connected to the door ensured that power was applied to the high voltage supply only when the door was shut. Should the door be suddenly opened, while the high voltage supply was on, the micro switch broke the circuit causing a high voltage switch to ground the components at high potential.

The voltage switch used as a safety switch was connected to ground through a 2 Mohm resistor chain. This resistor chain was present to ensure that no damage could occur to the switch from high currents. The switch could also be actuated at any time during an experiment to ground the equipment.

The safety mechanisms incorporated in the equipment are best described by a detailed circuit diagram (Figure 2).

A test point was connected in parallel with the capacitor and test cell (point P, Fig.2). Devices such as a voltmeter or oscilloscope could be connected to the test point for monitoring purposes. The 200 Mohm resistance connected between point P and the test point was made from 40, 5 Mohm carbon resistors connected in series. The resistor chain was contained in polyvinyl tubing filled with transformer oil. The oil prevented any breakdown external to the resistors.

2.3 Sample Handling Equipment

The sample handling equipment consisted of test cell, dry ice bath, gas sampling bulb, manometer tube, gas cylinder, and vacuum pump.

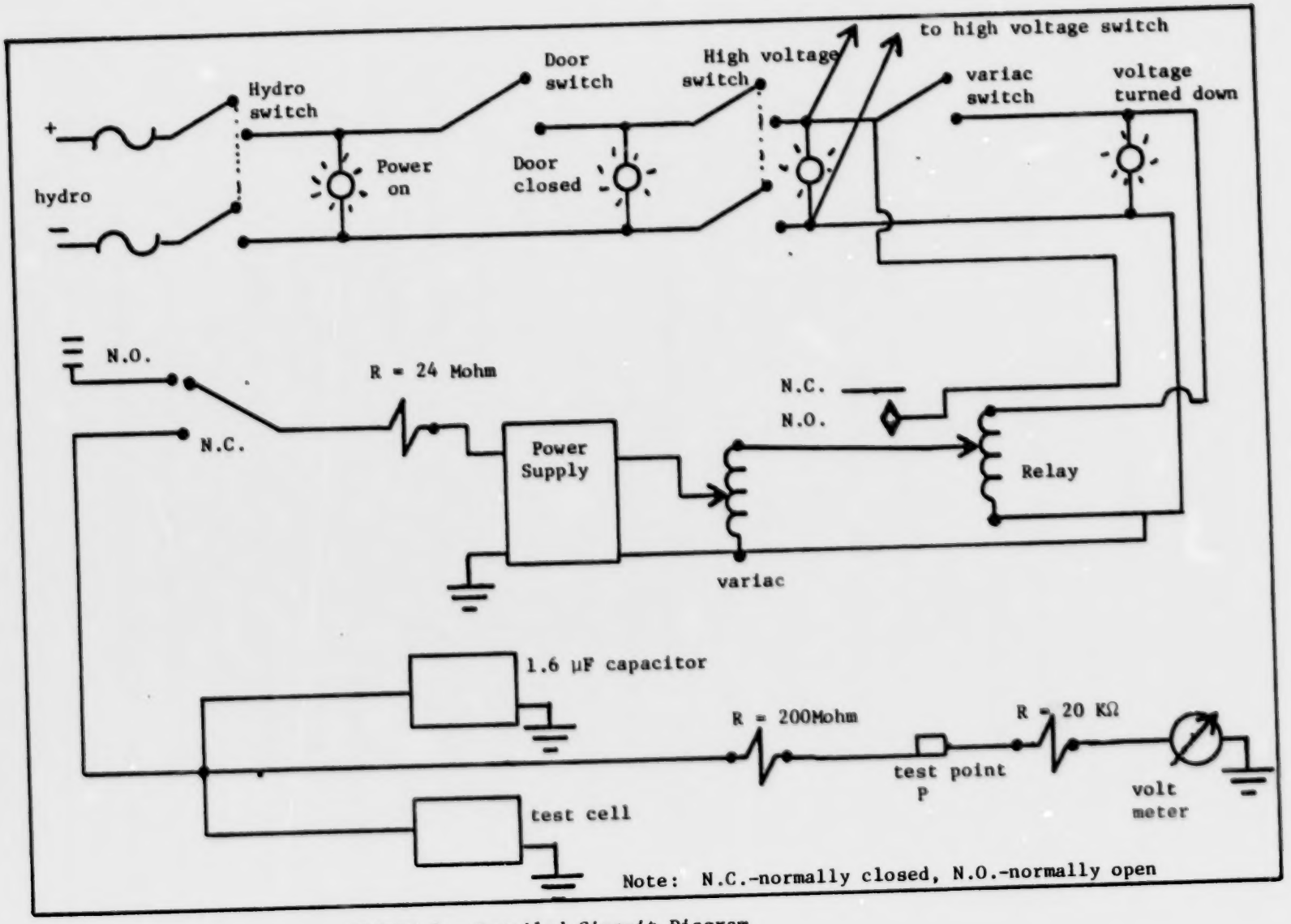

FIGURE 2: Detailed Circuit Diagram

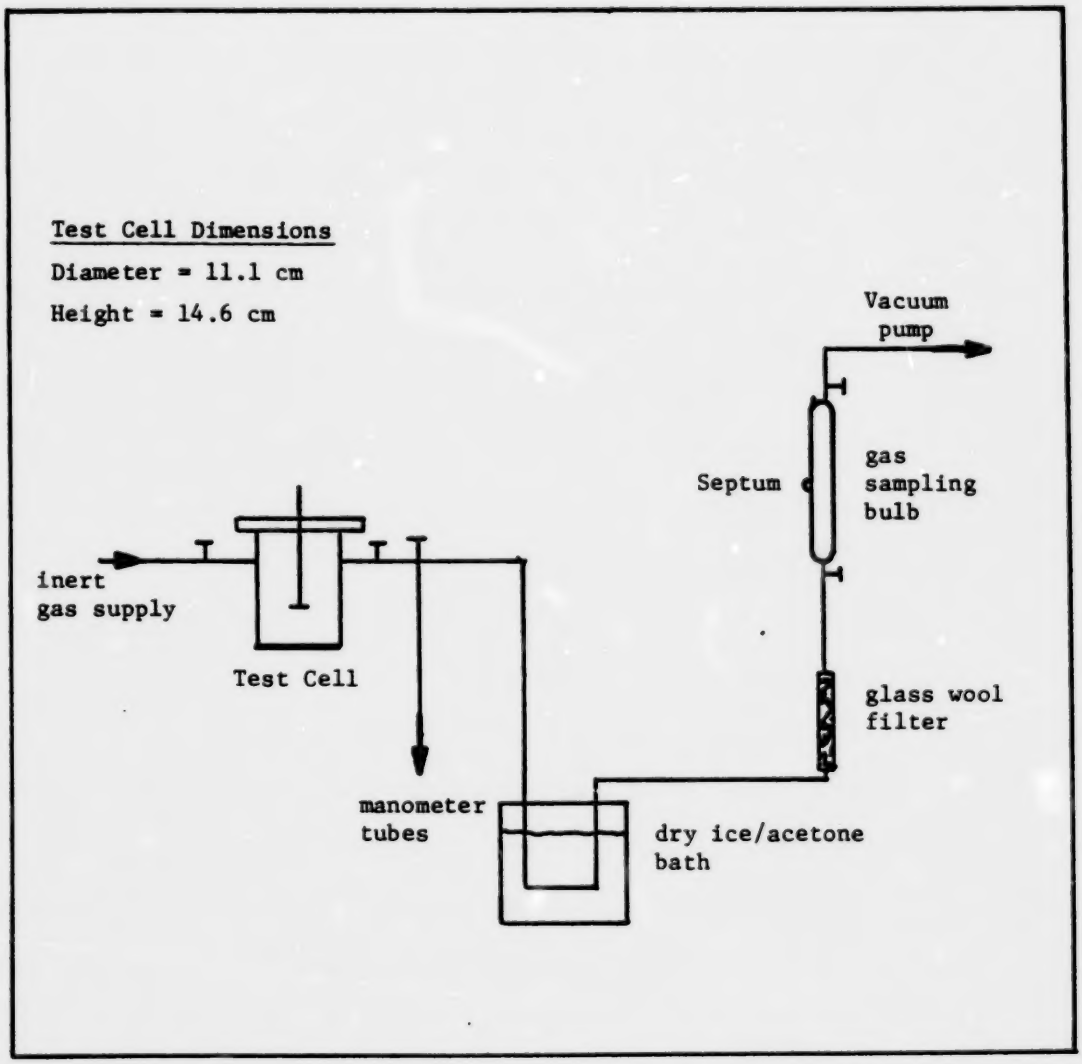

FIGURE 3: Sample Handling Equipment

The test cell, illustrated in Figure 3, was made from acrylic with the exception of the base which was aluminum. A brass disc fastened to the aluminum base was grounded. The cylindrical sampling bulbs made from glass had a 250 ml volume, glass stopcocks at each end and a septum port for withdrawal of gas samples via a syringe. A 54 cm long U shaped glass tube (6 mm ID) submersed in a dry-ice acetone slurry acted as a cold trap for condensibles in the gas samples. Two manometers, Merian fluid (S.G. 1) and mercury (S.G. 13.6), were used for pressure measurements. Figure 3 illustrates the experimental setup used most of the time for sample handling.

Electrode shape was changed depending upon the type of sample being tested. Cone shaped, round nosed, and flat faced electrodes were tried.

2.4 Gas Analysis Equipment

The gases from test samples were analyzed for content of hydrogen, carbon monoxide, carbon dioxide, methane, ethane, ethylene, and acetylene. A Carle Analytical Gas Chromatograph (model 111-H 197-A) interfaced with a Spectra Physics 4100 Computing Integrator was used for gas analysis. The Carle G.C. analizes all components except hydrogen in a thermal conductivity detector with helium as carrier gas. Hydrogen is eluted with the helium carrier

gas, but is then transferred by the HTS (Hydrogen Transfer System) into a nitrogen carrier before measurement.

Calibration of the gas chromatograph was undertaken before every set of analyses using a G.C. calibration gas purchased from Matheson of Canada Ltd. The gas analysis and maximum variance for the calibration gas composition are listed in Table 2.

2.5 Sample Composition

The biomass samples used in this project are listed in Table 3, along with their elemental analysis.[1]

The conductive additives used for pellet and string samples were Calgon Activated Carbon [2] and graphite powder (grade # 38) [3].

TABLE 2

G.C. Calibration Gas Composition

Component	Volume Percent
CH_4	5.14 ± .1%
O_2	.484 ± .01%
CO_2	11 ± .2%
H_2	11.3 ± .2%
C_2H_4	2.22 ± .04%
CO	4.1 ± .08%
Butene -1	.47 ± .01%
N_2	balance

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TABLE 3

Elemental Analysis of the
Biomass Samples

Substance	Mole % Dry Basis						Empirical Formula (Dry)
	C	H	O	S	N	Ash	
Cellulose AVICEL pH-102 100 μm	43.32	6.30	50.34	.001	.02	.03	$C_6H_{10.5}O_{5.22}$
Lignin (Indulin ATR)	65.5	5.4	27.2	1.7			$C_6H_{5.94}O_{10.2}$
Birch Wood 135 μm	48.66	6.37	44.33	.04	.1	.5	$C_6H_{9.4}O_{4.1}$

3 PROCEDURES

3.1 Samples

3.1.1 Pellet Samples

Pellet samples were made with a Carver bench top hydraulic press. The appropriate amounts of cellulose, graphite or activated carbon were weighed, mixed, then added to the die. A force of 10,000 lb was applied to the powder for 5 minutes.

3.1.2 String Samples

A water slurry containing activated carbon, graphite, additives or cellulose was prepared. The string was soaked in the slurry, then removed and placed in an oven at 60-100 degrees centigrade. Subsequently, layers of cellulose or conductive material were applied in a similar manner.

3.1.3 Wire Samples

The wire was first preheated with a 6 volt dc supply to remove any enamel. It was then cut to the desired length and dipped in LePages glue. When the excess glue had been removed the wire was rolled in the powdered sample and dried in an oven at 60 to 100 C. To increase the weight of sample on the wire, it was repeatedly dipped in a

water-biomass slurry and dried again.

3.2 Sample Setup

The sample was placed in the cell and connected to the electrodes. Wire and string samples were connected via alligator clips. Pellet samples were tested with flat head and pointed electrodes, made from brass.

The cell was purged with the carrier gas (Argon, Nitrogen or Hydrogen) for 5 to 10 minutes. The whole system was evacuated and then repressurized 3 to 5 times. Once this has been completed the system was left to equilibrate with respect to the temperature of the water bath. The sample in the cell was then ready for capacitor discharge.

3.3 Gas Sampling

The pressure increases associated with pyrolysis of the sample were generally in the range of 15 to 35 cm water. To take a gas sample after the discharge, the entire system, excluding the cell, was evacuated. Carrier gas was used to pressurize the cell to 5 psig, then the system and cell were connected by opening a valve. The pressurized gases flowed from the cell into the evacuated system, passing through a cold trap and into the sample

bulb. The bulb was then sealed, capturing the gas sample for subsequent analysis.

4 CHARACTERIZATION OF THE DISCHARGE

A considerable effort was made to characterize the capacitor discharge in the system. A Nicklette digital storage oscilloscope was connected to test point P, but the voltage readings were incomprehensible because distortion of the voltage trace occurred due to the inductive nature of the 200 Mohm resistance chain in series with P. However, from the oscilloscope readings the discharge time was estimated to be 70 micro seconds.

The nature of the discharge, ie. high current and voltage with a short discharge time, made it very difficult to make direct measurements. To reduce the current during discharge, resistors were connected in series with the capacitor and cell. A 1 ohm resistance wire, along with a voltage divider, was connected between the test cell and ground. This is illustrated in Figure 4. The voltage divider reduced the potential drop across the 1 ohm resistor by a factor of 10. The Nicklette scope was attached across the 1 ohm resistor, and measurements of the discharge were taken. Figure 5 shows traces generated during 4 KV discharges using 200, 300, or 400 ohm resistors between capacitor and cell. The ordinate scale is the estimated current of the spark. The maximum current increases when the resistance between capacitor and cell is

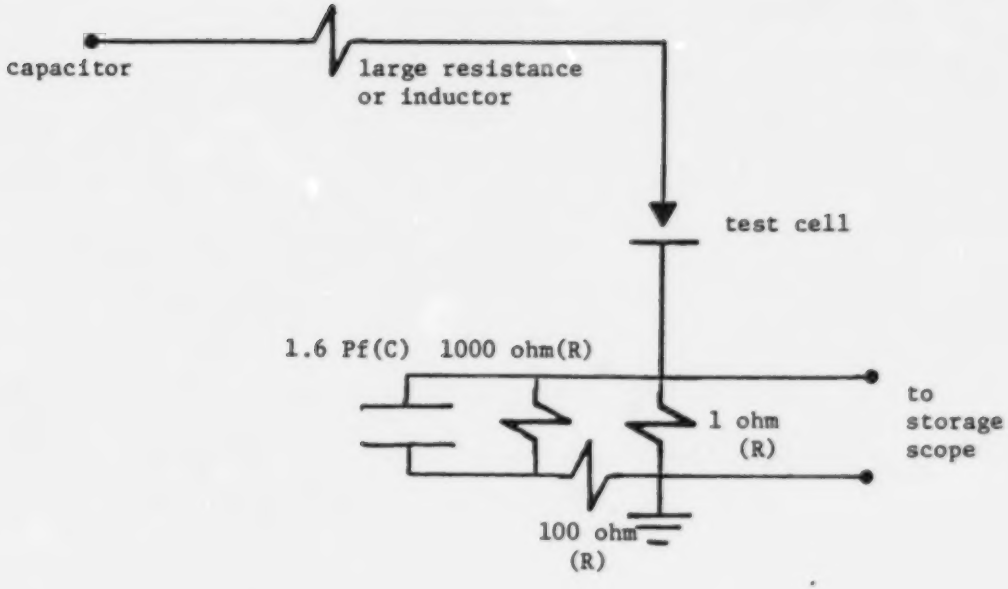


FIGURE 4: Illustration of 10 to 1 voltage divider

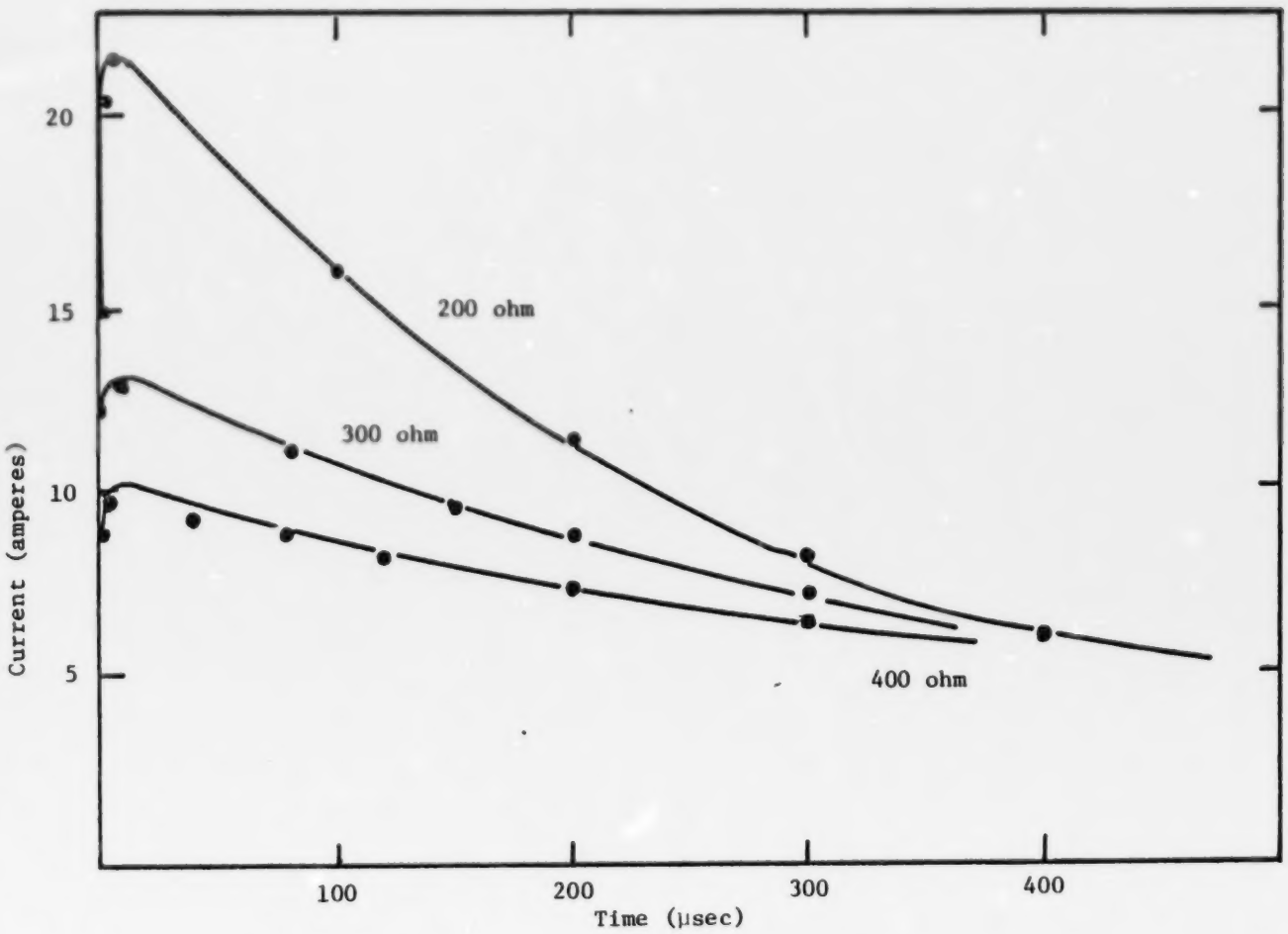


FIGURE 5: Current vs time for 4 KV discharges with 400, 300, and 200 ohm resistors in series with capacitor and test cell.

lowered. In this setup lowering the resistance below 200 ohms or increasing the discharge voltage was not possible because the resistors available were not able to handle the higher current and voltage. Therefore Figure 5 represents the best discharge obtainable with the resistors available. The discharge time has been lengthened to 200 usec from 70 μsec, but too much power was dissipated in the 200 to 400 ohm resistors between the capacitor and cell.

The inclusion of an inductor in series with the capacitor and cell served to reduce the peak current. An inductor was nesseccary to reduce peak currents during discharge, since the high voltage relay was rated at 600 amperes maximum current. The electrical setup for testing string and pellet samples contained the inductor. The combination of inductor and high voltage relay permitted discharges up to the maximum voltage (20 KV) across samples.

A 1 ohm resistor and voltage divider were again employed to measure the discharge. Figure 6 illustrates a 20 KV discharge with the inductor included in the circuit. The maximum current was 325 amperes. Somewhat lower currents would be expected with a sample between the electrodes.

Another desirable effect of the inductor was the

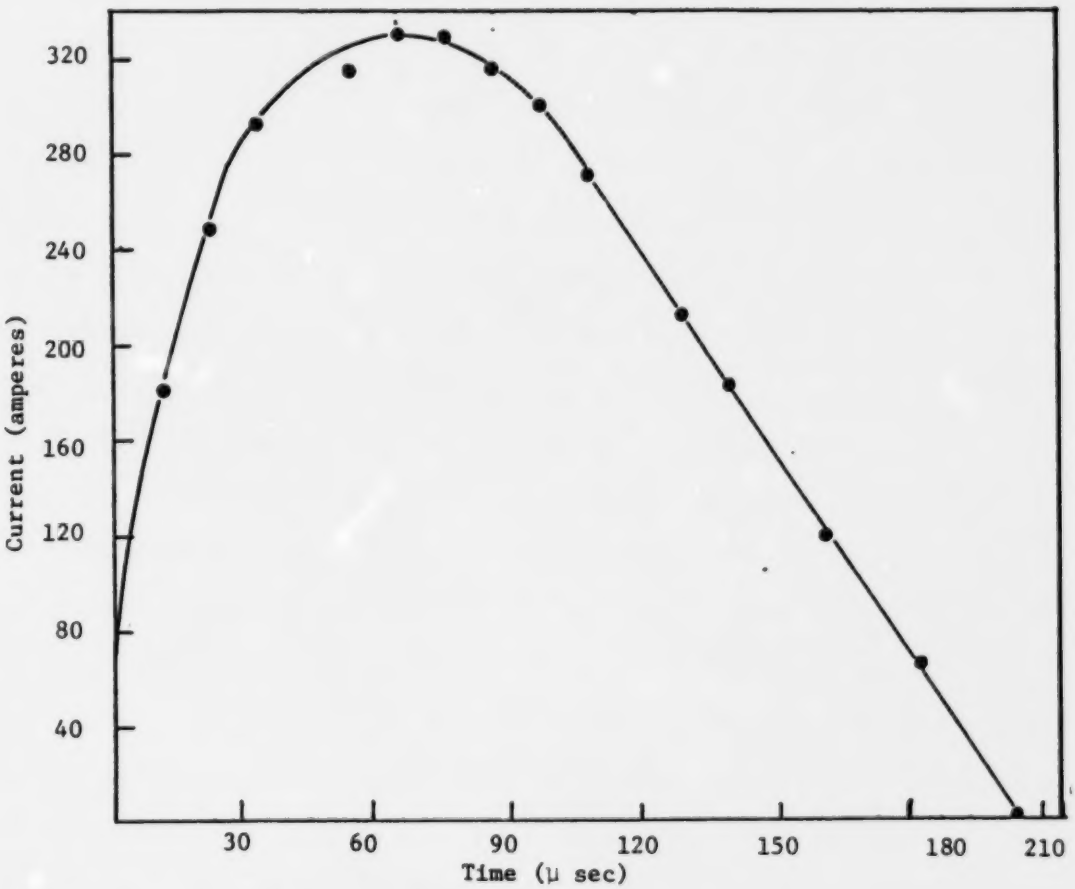


FIGURE 6: Discharge current versus time for a 20 KV discharge in test cell with inductor in series between capacitor and cell.

lengthening of the discharge time to 200 usec. However, there was a tradeoff because the inductor had a resistance of 35 ohms, and therefore a certain fraction of energy was lost in the inductor. As long as the sample 's resistance was large (> 100 ohms), less than a quarter of the energy was dissipated in the inductor.

In experiments using wire samples, the inductor and high voltage relay could not be used because the wire sample resistance (1-5 ohms) was very small compared to the resistance of the inductor. Discharging across the wire sample with the inductor in the circuit would have damaged the inductor. Therefore it was impossible to control peak currents, and thus it was difficult to characterize the discharge without the aid of a high voltage probe, which was not available.

5 EXPERIMENTAL RESULTS AND DISCUSSION: PELLITIZED SAMPLES

One phase of the experimental investigation focussed on pelletized samples . The pellets consisted of pure cellulose, or cellulose plus a conductive material such as activated carbon or graphite. A benchtop hydraulic press was used to compress the powdered samples into a disc shaped pellet. The dimensions of the pellets were 1.26 cm in diameter and between 6 cm and .05 cm thick. Pressures of up to 3000 atmospheres were transmitted by the hydraulic press to the powdered sample, producing an average final pellet density of 1.2 gm/cm3.

Initial testing using pelletized pure cellulose or wood dowelling indicated the electrical discharge was not causing appreciable pyrolysis of the sample. There appeared to be two mechanisms by which the discharge travelled to ground. One, the current flowed around the sample, conducted by the air; and in the second case, the discharge occurred through the sample, causing it to split apart due to the shock wave generated. The samples of wood dowelling (Table 4) were split apart by the discharge but little or no pyrolysis took place. It was thought that an improvement in the conductance of the pellet might eliminate both mechanisms and allow the biomass material itself to pass the electricity to ground.

TABLE 4

Wood Dowel Samples

Sample Height (mm)	Electrode[A] Penetration (mm)	Discharge Voltage (KV)	Pressure Increase (mmHg)	Sample wt (gm)	Unrecovered Sample (gm)
4	2	1.6	0	.3339	.0023
10	3	3	3	.7991	.005
14	3	4	2	1.1241	.0089
17.5	2.5	4	0	1.1443	.0041

A) Top Electrode: pointed tip penetrating into sample

Note: wood dowel used had a diameter of ≈ 12.0 mm

Atmosphere: Argon at atmospheric pressure

Pellet samples made from activated carbon or graphite and cellulose showed improved conductivity compared to pure cellulose pellets. The physical characteristics of these pellets are presented in Table 5 and Table 6. The values for resistivity are calculated from the measured resistance (R), thickness (L) and cross sectional area (A) of the pellet , using equation 5.1.

$$p = A*R/L \qquad 5.1$$

The resistance measurements were taken by putting the pellet in the test cell and placing the electrode on top of the sample. An electronic multimeter was used for the measurements, taking 3 to 6 readings per sample. For comparison the resistivity of wood and copper are 10 exp 11 and 10 exp -5 ohm/mm respectively.

The data from Tables 5 and 6 are represented in Figure 7. The plot illustrates the greater conductivity of the graphite-cellulose pellets over the activated carbon-cellulose pellets.

The observations from tests performed on pelletized samples are presented in Tables 4, 7, and 8. The wood dowel samples were split during discharge. The electricity

TABLE 5

Activated Carbon and Cellulose Pellets

wt% Carbon	Thickness mm	Resistance ohms	Resistivity ohm·mm
15	3.2	∞	∞
17.9	3.14	∞	∞
21.1	3.71	4,203	143,500
25.4	3.73	312	10,596
31.3	4.1	61.7	1,906.0
32.1	4.09	108.7	3,366.0
36.6	4.52	63.3	1,774
49.8	4.82	12.0	315
61.3	5.28	8.3	200

Note: Diameter of the pellets was 1.26 cm

All measurements were made at room temperature

TABLE 6

Graphite and Cellulose Pellets

wt% Graphite	Thickness mm	Resistance ohms	Resistivity ohms mm
100	6.2	<.1	2.0
80	3.7	.2	6.9
60	2.3	.3	16.3
50	3.2	.6	24.0
	5.7	.3	6.0
40	3.0	.2	8.5
	5.7	.5	11.1
30	3.0	.5	20.8
	5.8	.7	15.2
20	2.4	1.7	90.2
	4.7	2.2	60.0
10	5.1	28	699.0

Note: Diameter of the pellets was 12.6 mm

All measurements were made at room temperature

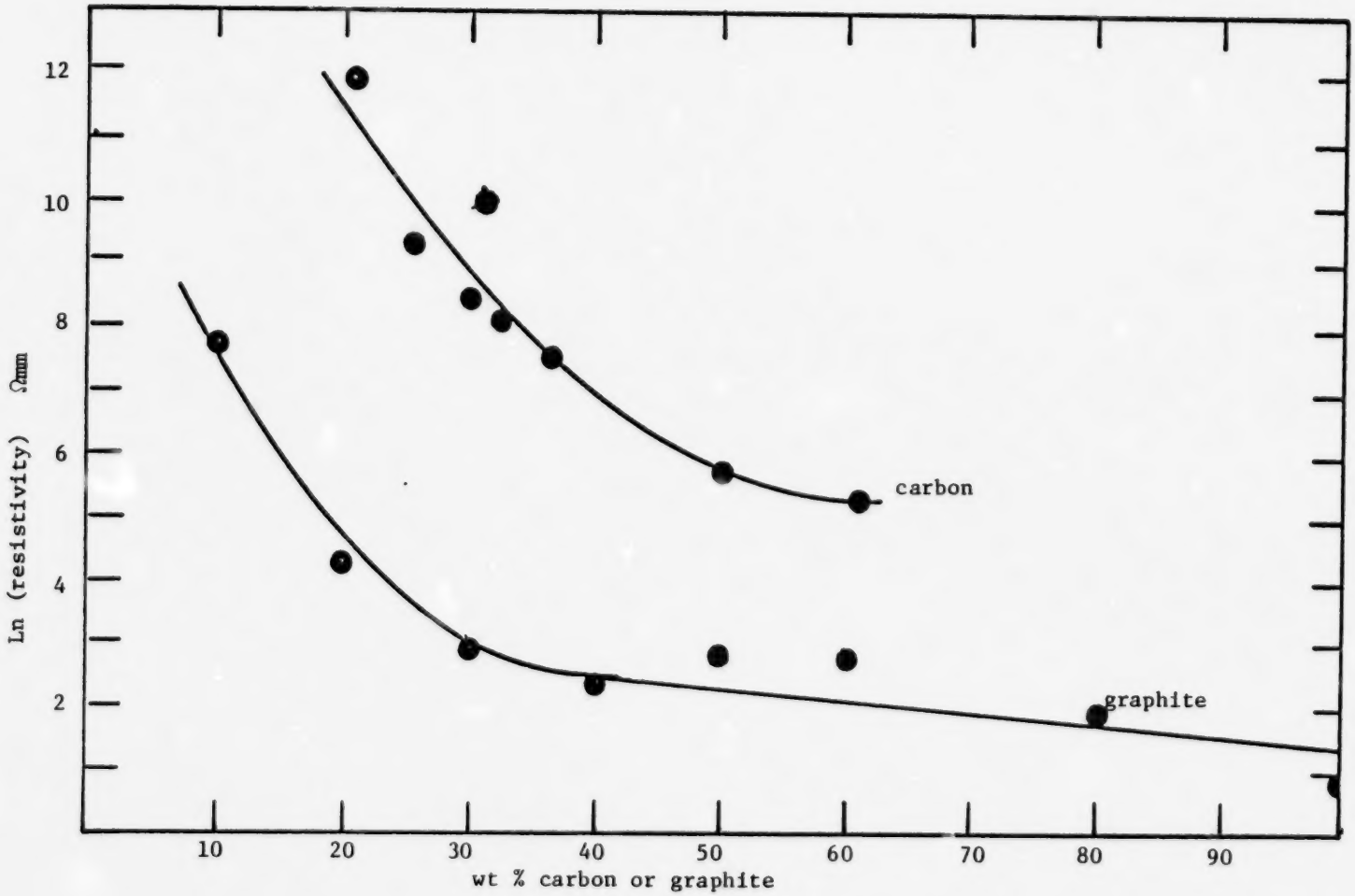


FIGURE 7: Resistivity versus weight percent carbon or graphite in 1/2" diameter pellets (balance of material is cellulose).

passed through the sample but little pyrolysis took place, which is evident from the negligible pressure rises and the low amounts of sample unrecovered.

The activated carbon-cellulose pellets also showed very low pressure increases as well as no visual evidence of pyrolysis or significant production of gases. Graphite-cellulose pellets behaved in the same manner.

In only a few of the experiments with pelletized samples did the discharge shatter or split the sample. This indicates that more frequently the discharge travelled through the air, around the sample. It was therefore concluded that the cell atmosphere offered a more conductive path to ground than the sample. This is a reasonable conclusion because at the time of discharge or breakdown the resistance of a gas virtually, instantaneously changes from almost infinite to negligible.

A comparison was made of the voltage-time curve between discharge without a sample and discharge across graphite pellets. The two voltage-time curves were found to be essentially identical. This was true both for cases where the sample had split apart and when the discharge appeared to pass around the sample. Apparently the biomass did not transmit the electricity in either case, and thus resistive heating in the pellet did not take place.

TABLE 7

Activated Carbon - Cellulose Pellet Samples

Pellet Weight (gm)	Weight % Carbon	Discharge Voltage KV	Observed Pressure Increase mmHg
.5806	28	10	4
.5956	38	10	5
.6621	54	10	5

Note: The above samples were tested in an Argon atmosphere a 610 mmHg vacuum. The pellet size is 12.8 in diameter. The thickness of the pellets were <4 mm.

TABLE 8

Graphite - Cellulose Pellet Samples

Pellet Weight (gm)	Pellet Resistance (ohm)	Pellet Thickness (mm)	Discharge Voltage (KV)	Pressure Increase (mmHg)	Unrecovered Weight (gm)
1.2202	∞	7.9	20	0	0
.7823	117	6.4	20	0	.0012
1.1908	146	7.9	20	5	.0018
5.8472	189	32	20	5	.004
4.2891	250	22	16	0	.0195

Note: Diameter of the pellets are 1.26 cm

The atmosphere is air at 1 atm pressure

A larger separation between electrodes was tried by using thick pellets, but this also failed to stop the discharge from travelling through the air. At the same electrode separation, without a sample in place, no discharge would occur. Apparently, the sample had an effect on whether or not discharge occurred, but the discharge had no measurable effect on the sample.

6 EXPERIMENTAL RESULTS AND DISCUSSION: CONDUCTIVE STRING SAMPLES

The second type of sample to be investigated was ordinary household string. The string provided a very different sample geometry, ie. long and narrow, compared to the short and wide pellets. The longer the sample, the greater the electrode separation distance, thus reducing the possibility of a discharge bypassing the sample to ground.

Initial testing on water-soaked string proved that discharges through the string were capable of evaporating the water. This only occurred when sufficent water was present to ensure electrical continuity between the two electrodes attached to the ends of the string.

Subsequently an activated carbon-water slurry was used to coat the string samples with a conductive material. The strings were then dried in an oven at 100 degrees centigrade for 1 hour. This produced string samples with resistances of about .62 Mohm/cm (see Table 9). Replacing activated carbon with graphite lowered the string resistance to 2.6 kohm/cm. Increasing the weight of graphite dried on the string resulted in resistance values of 5oo ohm/cm. However, the samples were very brittle and

TABLE 9

Resistance of String Samples

Sample Composition weight percent	length[A] (cm)	Resistance ohm	Resistance/L ohm/cm
80% string, 20% graphite	5.1	13 K	2.6 K
50% string, 50% activated carbon	10.2	6.3 M	.62 M
[B]String painted with TV Tube paint	5.1	11 K	2.2 K
[B]Silicone based graphite past on string	6.4	12 K	1.9 K
56% string, 44% graphite oil paste	5.1	38 K	7.5 K
50% string, 25% graphite, 25% cellulose	6.4	3.2 K	500
52% string, 45% graphite, 3% sugar	6.4	2.4 K	375
[B]10% Na-alginate, 90% graphite coating	7.6	360	47
[B]10% Agar, 90% graphite coating	10.2	2.4 K	24
[B]10% dexatran, 90% Graphite coating	7.6	450	59

(A) The diameter of the string was approximately 1.6 mm.

(B) The weight % of the string in the sample was not measured for this case.

difficult to work with. The brittleness of the samples was corrected by the addition, in small amounts, of high molecular weight sugars or alginates. The results can be found in Table 9. These additives not only gave the sample strength but improved the homogeneity of the coating and lowered the resistance to 24 ohm/cm.

The activated carbon-cellulose string samples showed little evidence of combusion or gasification in an air atmosphere. Table 10 shows three runs where low pressure increases were observed with no evidence of pyrolysis gases being produced.

The graphite-cellulose string samples tested in air intially showed promise. There was evidence of combustion, a larger pressure rise and substantial loss of sample weight. Runs 1 to 4 in Table 11 illustrate the results with graphite samples tested in an air atmosphere. However, run no. 5 was performed at a reduced pressure and gave no evidence of gasification.

Cellulose-graphite string samples tested in an argon atmosphere showed no evidence of pyrolysis (Runs 6 to 9, Table 11). These results discouraged any further testing using carbon- or graphite -impregnated string samples. Also, a comparison of the voltage-time curves between a discharge through a 3 inch graphite string sample (R = 413

TABLE 10

20 KV Discharge Through
Activated Carbon-Cellulose String Samples
In an Air Atmosphere

Sample Weight gm (A)	Initial Pressure mmHgA	Pressure Increase mmHg	Evidence of Gases formed (B)	Weight of Unrecovered Sample(gm)
.1440	74.0	6	NO	.0318
.0966	760	4	NO	.0152
.0713	99	2	NO	.0015
.0997	48.4	6	YES	.0093

A) Sample length was approximately 5.1 cm, and the resistance of the samples were approximately 3 to 9 M ohms.

B) Evidence of gases formed was a visual observation recorded during experimentation.

TABLE 11

20 KV Discharge Through Graphite-
Cellulose String Samples 7.6 cm long

Sample	Sample wt (gm)	Sample Resistance (ohm)	Initial Pressure mmHg	Pressure Increase mmHg	Evidence of Gases formed (A)	Unrecovered Sample wt (gm)
Air Atmosphere						
1	0.3432	1.1KΩ	atm	15	yes	.0384
2	0.3379	113	atm	10	yes	.0360
3	0.4932	314	atm	10	yes	.0545
4	0.3051	100	atm	8	yes	.0252
5	0.3007	140	650vac.	0	no	.0054
Argon Atmosphere						
6	0.6043	126	662vac.	5	no	.0081
7	0.5391	129	atm	6	no	.0033
8	0.3078	126	atm	4	no	N.A.
9	0.5563	194	142	0	no	0.0

(A) Evidence of gases formed is a visual observation recorded during experimentation.

Note: All string samples were 7.5 cm long.

ohm) and discharge without a sample (electrodes were in physical contact), showed that the sample offered only 5.6 ohm of resistance during discharge. There can be little resistive heating when the sample only impedes the current with a resistance value approximately 14 percent of the total resistance between the capacitor and ground. Total impedence is the sum of the inductor and the actual sample resistance. Like the pellet samples, the string samples helped initiate discharge but were unaffected by it, when in an inert atmosphere.

7 EXPERIMENTAL RESULTS AND DISCUSSION: COATED WIRE SAMPLES

A metal wire has similar geometry to the string samples but it is made from a highly conductive material. If the wire is very thin, 10/1000 of an inch, the resistance of the wire will be sufficiently high to dissipate the electrical energy as heat. Cellulose surrounding the wire could be rapidly pyrolyzed from the heat dissipated in the wire. Cellulose was applied on the wire as a wet slurry, then dried to form a hardened layer.

Preliminary results, Table 12, showed some success. Two resistance wires (5.4 ohm/m and 1.3 ohm/ m) were used. The best result was obtained with sample No. 5, where the highest pressure increase was observed. The wire itself was totally volatilized during the electrical discharge of the capacitor.

It should be noted that at this point in the investigation a temperature controlled water bath was used to prevent any fluctuations or changes in pressure in the test cell due to temperature changes.

TABLE 12

Preliminary Results for Coated Wire Samples

Sample No.	Length cm	Resistance Ω	Cellulose wt (gm)	ΔP cm H_2O
Wire A				
1	15	10.6	.0244	3.5
2	15	9.6	.0332	3
Wire B				
3	15	2.6	.0406	7.4
4	30	4.7	.0387	4.5
5	30	4.7	.0385	4.5

Conditions: Temperature = 30.1°C, Pressure = 1 atm argon

A nylon insulation covered wire ∴ Cellulose wt = cellulose + insulation
Wire A has D = 0.1 mm, R =5.4Ω/m Manganin
Wire B has D = 0.2 mm, R =0.3 Ω/m Manganin

7.1 The Bare Wire Phenomenon

An unexpected pressure increase due to the volatilization of the bare wire was observed. Several methods of wire pretreatment were tried to eliminate this pressure increase. Table 13 shows results from a number of samples that were pretreated by either a furnace at 600 degrees or a battery charger providing current through the wire until it reached a red hot state. The pressure increase, P, is from the discharge of the capacitor across the pretreated wire. Sample no. 7 was untreated and showed the highest pressure increase. The best results were achieved with the plain steel wire pretreated by the battery charger.

It is assumed preheating vapourized any enamel or residue on the wire surface, although there still was a small pressure increase after discharge across a treated wire, which cannot be explained.

Pretreatment by the battery charger was important to minimize experimental error, therefore the technique was used for ever sample. A 0.15 mm diameter steel piano wire 76 mm long was chosen as the standard.

TABLE 13

Pretreatment of Bare Wire

Sample No.	Length mm	Pretreatment method before Discharge	ΔP cm H_2O
Wire B			
1	76.2	Battery Charger	3.1
2	76.2	furnace	1.6
3	76.2	furnace	1.2
4	38.3	furnace	1.2
5	101.6	furnace	1.1
6	38.3	furnace	.9
7	152.4	none	3.8
Wire C			
8	76.2	Battery Charger	.5
9	76.2	Battery Charger	1.2
10	76.2	Battery Charger	.4
11	38.3	furnace	1
12	127.0	furnace	3.0
13	25.4	Battery Charger	.9

Wire B has D = .008 in, R = 4.5Ω/ft, Manganin

Wire C has D = .008 in, R = 2.8Ω/ft steel piano wire

Conditions: Temperature 30.1°C, pressure atmospheric argon

7.2 Pressure Increase Versus the Mass of Material On the Wire

The relationship between pressure increase and weight of cellulose and glue on the standard wire was investigated. The glue was applied to the bare wire as a thin coating to help the cellulose powder adhere. The dry weight of glue needed for a 76 mm wire was approximately .006 grams. After the first layer of cellulose had dried, subsequent layers were applied by dipping the wire into a cellulose-water slurry. The water was evaporated at 60 to 80 degrees centigrade. This step was repeated until the desired sample weight had been obtained.

Two curves are presented in Figure 8 corresponding to two heating methods. A 6 volt dc power supply was used for slow pyrolysis and the capacitor discharge for flash pyrolysis. The slow heating technique involved heating times greater than one minute.

The results are presented as a plot of pressure change versus weight of cellulose plus glue on the wire. A straight line was fitted to the slow pyrolysis data by least squares. Larger pressure increases were observed with slow pyrolysis than with flash pyrolysis. The slow method completly pyrolyzed all the cellulose into gas and tar, leaving a small amount of char on the wire.

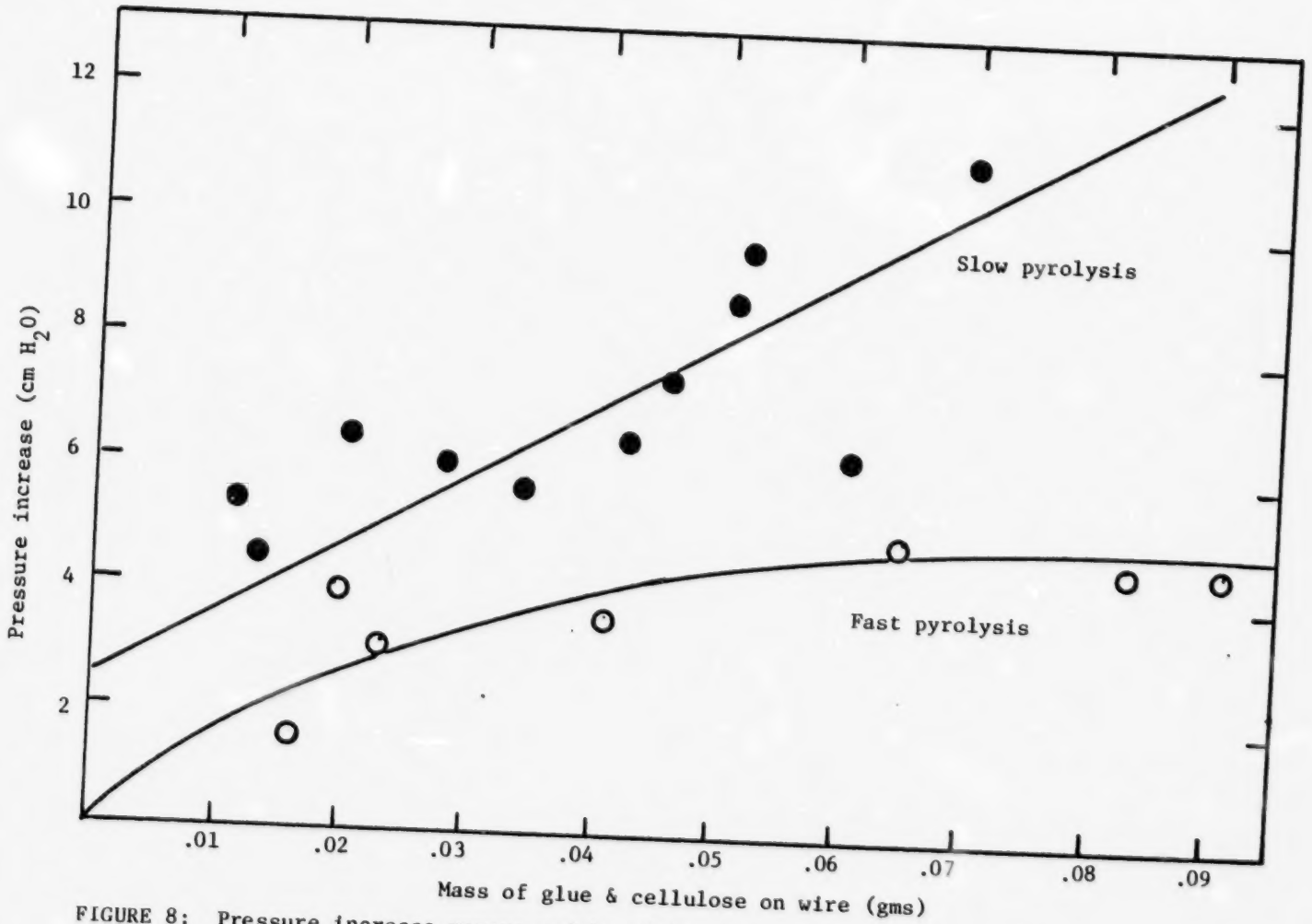


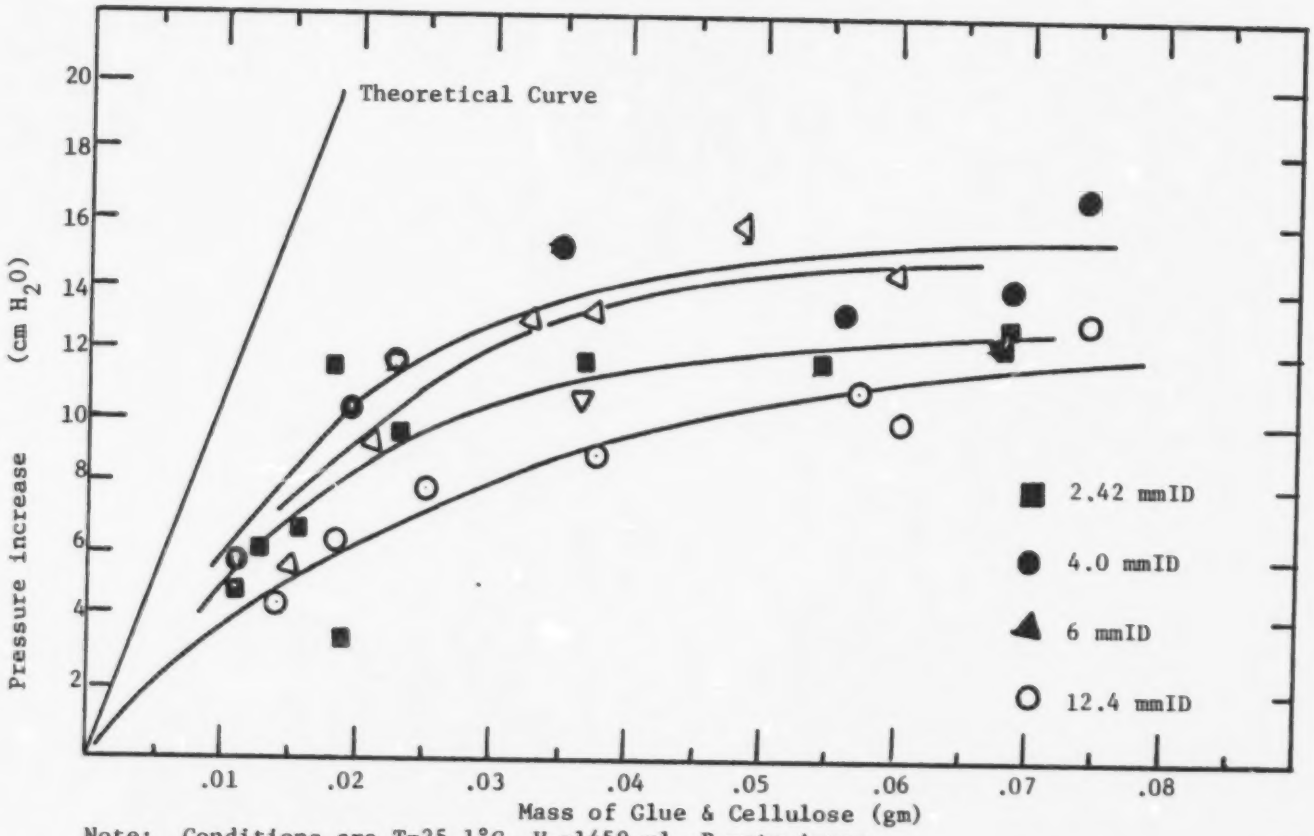
FIGURE 8: Pressure increase versus weight of biomass on wire 76mm long, .15mm wire, Argon atmosphere, T=30°C, Volume=1459 ml.

The flash pyrolysis experiments gave lower gas yields, with the yield approaching a constant 4-5 cm water pressure increase when the weight of cellulose on the wire was greater than .06 grams. This levelling off is believed to be due to the fact that the outer layers of biomass were blown off by the shock wave and hence this material did not contact hot plasma.

The pressure increases associated with the flash pyrolysis runs were very small. A glass tube surrounding the wire sample during discharge enhanced the contact between hot plasma and biomass. The improved contact resulted in a higher pressure increase, and thus more conversion of the sample to gases. Glass tubes with inners diameters of 2.4, 4.0, 6.0, and 12.4 mm were studied for their effects on pressure increase, as a function of sample weight. Results are illustrated in Figure 9, which shows that 4 or 6 mm ID glass tube caused the largest ΔP's. All experiments involving containment tubes showed pressure increases above those observed without tubes.

The theoretical curve shown in Figure 9 is based on total conversion of the cellulose and glue, yielding a product gas having a composition as observed in our runs. This neglects any tars or water formed.

For a given amount of pyrolysis, the pressure increase



Note: Conditions are T=25.1°C, V_C=1459 ml, P_O=atm Argon

FIGURE 9: Effect of glass containment tubes on pressure increase

from pyrolysis is proportional to the volume of the test cell. A spacer was placed in the test cell to reduce its volume and hence increase experimental accuracy.

7.3 Gas Analysis

7.3.1 Fast and Slow Pyrolysis In An Argon Atmosphere

Table 14 shows the gas analysis results obtained from biomass-coated wire samples in an argon atmosphere. Water and tar were removed by freezing in a dry ice/acetone bath followed by a glass wool filter. The figures have been normalized on the basis of the combined volumes of the gases listed.

The flash pyrolysis runs resulted in relatively high concentrations of hydrogen and carbon monoxide, whereas slow pyrolysis yielded much carbon monoxide and carbon dioxide with little hydrogen. The slow pyrolysis p oduct composition reflects the mild reaction conditions. The hydrogen in the cellulose was contained after pyrolysis in the tarry substance present on the cell walls and in the water vapour produced.

Small quantities of hydrocarbons were found in a few runs, but it appears they were not concentrated enough to be detectable in all the runs. Apparently runs with a very low P did not provide enough pyrolysis gas in the sample

TABLE 14

Analysis of Gases from Pyrolysis Runs in an Argon Atmosphere

Biomass-Soaked Wire Samples

Run Number	1	2	3	7	8	9	10	11	12	13
Flash or Slow	F	F	S	S	S	S	F	F	S	S
P (cm water)	6.0	4.5	15.2	4.5	5.5	6.5	9.5	9.6	11.3	24
Cell Volume (cm^3)	1500	521	521	521	1500	1500	521	521	521	521
Mass of glue & cellulose	.0466	.0352	.0492	.0428	.0245	.0562	.0303	.0715	.0621	.0721
Volume % of gases (H_2)	70.1	40	22.4	5.3	0.0	0.0	46.1	47.2	5.2	23.8
CO	29.9	.52	49.3	41.4	81.1	81.9	40.8	47.2	49.3	55.7
CO_2	0	0	20.3	51.3	18.9	18.1	0	0	49.5	13.7
CH_4	0	0	6.1	2.1	0	0	5.7	0	2.0	4.6
C_2H_6	0	0	0	0	0	0	1.0	0	1.0	0
C_2H_4	0	0	1.9	0	0	0	3.6	0	0	2.2
C_2H_2	0	8.8	0	0	0	0	2.9	5.7	0	0
Gas Mass[A]/ Cellulose Mass (%)	2.61	4.54	16.4	6.83	39.2	20.8	9.02	3.94	8.75	16.06

A Gas mass does not include water

to have all constituents of the gas detectable. Note the improvement in the gas analysis when the cell volume was decreased from 1500 ml to 521 ml.

7.3.2 Fast Pyrolysis In A Nitrogen Atmosphere

The experimental results from fast pyrolysis of wire samples in a nitrogen atmosphere are given in Table 15 and Table 16. The gas composition for cellulose samples was very stable and did not appear to be a function of the tube size or mass of cellulose on the wire. Again, note the very low carbon dioxide concentrations. In runs 14, 19-21 and 23-24 hydrocarbons were not detected due to the low P, hence the low concentration of these gases. It appears hydrogen may have leaked out of the sample bulb in run no. 18, possibly through the rubber septum.

Runs 15-17, 25 and 27-31 were used for calculation of a mean gas composition from cellulose samples. The mean gas composition along with one standard deviation above and below the mean is illustrated in Figure 10.

The gas composition from lignin and birch flour differed from that with cellulose. Lignin samples, runs 35-37, show a decrease in the hydrogen concentration and larger quantities of hydrocarbons, especially acetylene. Two of the three lignin runs show significant differences

TABLE 15

Experimental Results: Gas Analysis for Cellulose Samples using a Containment Tube and a Nitrogen Atmosphere

Run Number	14[A]	15[A]	16[A]	17[A]	18[B]	19[B]	20	21	22[C]	23[D]	24[E]	25[E]	26[f]	27[f]	28[f]	29[G]	30[G]	31[G]
P cm water	2.4	14.1	19.3	37.7	3.0	7.4	16	6.2	11.2	11	12.6	16.5	18	31.8	35.8	32.2	32.2	25.1
Cell Volume ml	1458	1458	521	521	1458	1458	521	1458	1458	1458	1458	1458	521	521	521	521	521	521
Mass of Cellulose & glue gm	.0512	.068	.0145	.0684	.0428	.0455	.0947	.0940	.1055	.0605	.0232	.1054	.015	.0367	.1243	.0333	.0757	.0656
H_2 (%)		48.8	46.7	46.2		56.5	51.7	54.1	49.7	53.2	52.1	50	48.5	46.3	45.1	46.5	45.6	46.8
CO	66.4	47.5	51.4	50.1	72.3	42.4	47.5	45.9	47.8	46.0	47.2	45.8	50.8	50.2	49.9	49.9	50.3	48.6
CO_2	24.1	1.0	.8	.8	28.0	1.2	.8		1.0	.8	.8	.9	.6	.7	1.1	.8	1.0	1.1
CH_4		1.2	.8	1.3								1.6		1.2	1.4	1.2	1.5	1.7
C_2H_6																		
C_2H_4														.4	.5	.3	.4	.5
C_2H_2		1.4	.7	1.5					1.5			1.8		1.2	1.9	1.3	1.2	1.3
Gas mass gm	.004	.0125	.0063	.0124	.0056	.0058	.0048	.0049	.0098	.0091	.011	.0142	.0057	.0104	.0120	.0105	.0107	.0066

Note: All conditions unless specified are T_o = 25°C, P_o = 1 atm (N_2)
Tube sizes surrounding sample are: A = 2.42 mmID, B = 1.66 mmID, C = 8 mmID, D = 12.47 mmID, E = 4.00 mmID, f = 6.0 mmID, G = 4.82 mmID.

TABLE 16

Experimental Results: Gas Analysis of Samples in a Nitrogen Atmosphere

Run Number	58[A]	59[A]	35	36	37	38	39	40	60[A]
ΔP cm H_2O	33	30.7	17.4	31.3	33	34.1	22.2	39.1	20.4
Sample	cell	cell	Lig	Lig	Lig	BF	BF	BF	BF
Sample wt & glue (gm)	.0763	.0584	.014	.0582	.0610	.0429	.0953	.0824	.0784
Vol % of gases H_2	45.17	45.55	45.5	37.5	37.8	40.1	43.2	39.2	41.5
CO	50.24	49.95	47.7	46.1	45.1	50.4	47.3	50.0	49.3
CO_2	1.23	1.05	.6	1.4	1.4	1.4	1.8	1.6	1.9
CH_4	1.66	1.87	0	3.2	3.9	3.0	3.1	3.7	3.5
C_2H_4	.47	.48	0	1.0	1.2	.9	1.3	1.3	1.2
C_2H_2	1.23	1.10	6.3	10.9	10.8	3.5	3.3	4.6	2.6

Note: All conditions unless specified are T = 25°C, P_o = 1 atm (N_2), V_c = 521 ml, 3" wire samples, 4 mm ID glass tube surrounding sample.

A = tube ends were plugged with room temperature vulcanizing agent (RTV)

in gas composition compared to the mean cellulose product distribution(see Figure 10).

Graef [4] observed a product distribution of 43% hydrogen, 44% carbon monoxide, 14% acetylene, 2% carbon dioxide and 2% methane, from microwave plasma pyrolysis of lignin. Note the similarity in gas composition between microwave plasma and electrical discharge pyrolysis. In conventional thermal pyrolysis systems, methane is a large fraction of the product gases, whereas acetylene is less than 3 % by volume [5]. The high concentrations of acetylene observed from our experiments indicates very high localized temperatatures.

The birch flour runs yielded lower hydrogen and higher carbon monoxide concentrations and larger amounts of acetylene and methane compared to cellulose runs. These differences can be observed in Figure 10, which shows a comparison of pyrolysis gas composition emanating from the three substrates. The birch flour gas fractions lie outside the range of one standard deviation from the mean cellulose composition.

All three biomass samples yielded pyrolysis gases indicative of reaction temperatures greater than 1000 degrees. According to Graham [6], greater than 85 percent of the biomass feed is converted primarily to carbon

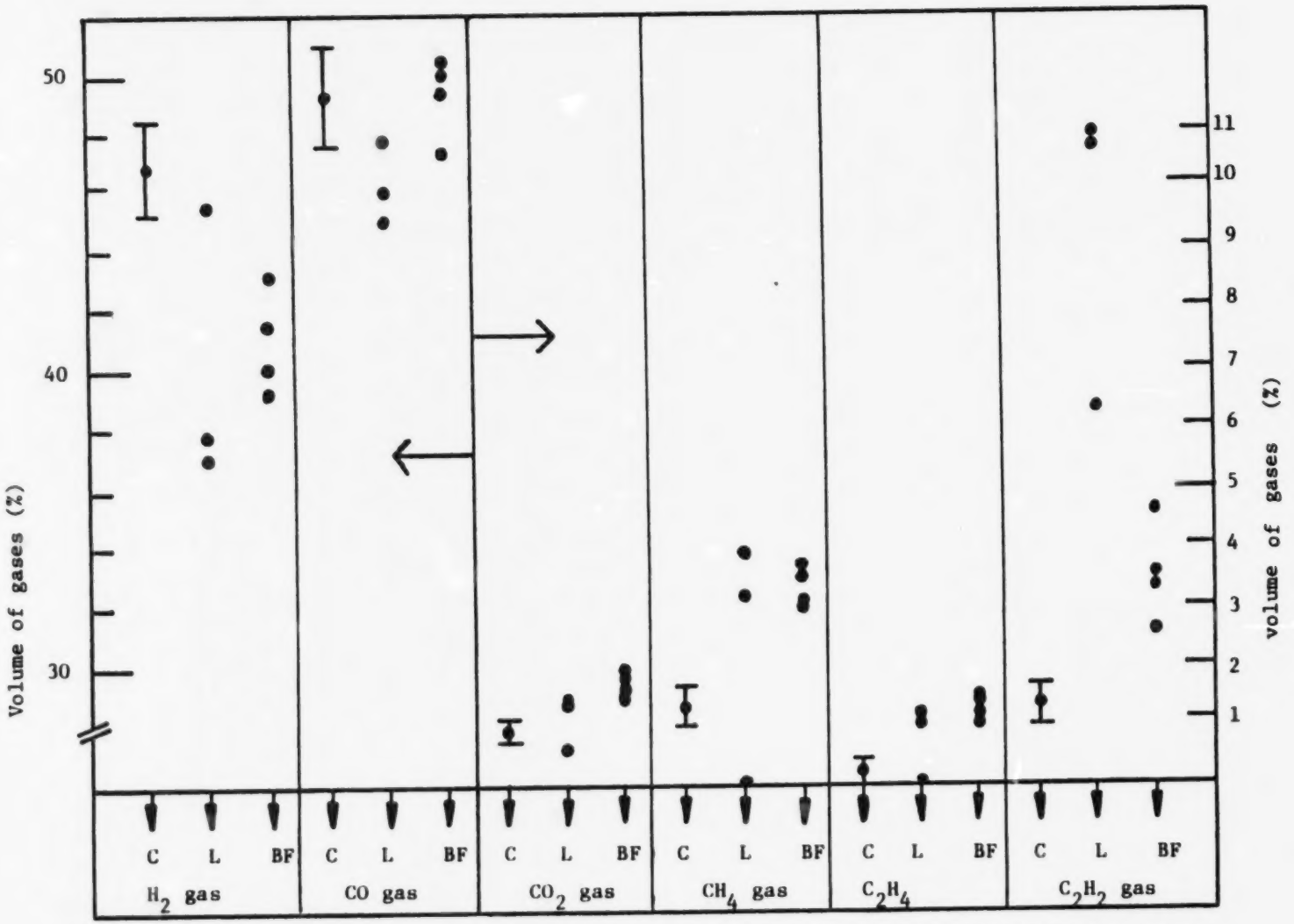


FIGURE 10: Comparison between mean cellulose product composition (C) and individual Lignin (L) or Birch Flour (BF) gas product compositions.

monoxide and hydrogen at temperatures approaching 1000 degrees.

7.3.3 Fast Pyrolysis of Moist Samples In A Nitrogen Atmosphere

Water was added to dried samples before pyrolysis. The effects of the water on gas composition for cellulose, lignin and birch flour samples is presented in Table 17. Generally the results show a reduction in carbon monoxide, coupled with a substaintial increase in hydrogen and carbon dioxide concentrations. These oservations can be attributed, in part, to the water gas shift reaction being shifted towards formation of carbon dioxide and hydrogen from water and carbon monoxide.

7.3.4 Fast Pyrolysis In A Hydrogen Atmosphere

The atmosphere in the cell was changed to hydrogen. Results, shown in Table 18, are normalized on the basis of the combined volumes of carbon monoxide, carbon dioxide, methane, ethylene and acetylene. Runs 25, 36 and 38 in Table 18 were samples pyrolyzed in nitrogen. A comparison between runs 25, 36 and 38 and their counterparts in a hydrogen atmosphere shows no significant differences. The gas composition seems to be unaffected by the presence of hydrogen in the cell atmosphere.

TABLE 17

Experimental Results: Moist Samples in a Nitrogen Atmosphere

Run Number	32	33	34	41	42[A]	43[A]	44	45
ΔP cm H_2O	37.9	38.6	38.5	39.9	37	28.8	34.6	39.8
Sample	cell	cell	cell	Lig	Lig	Lig	BF	BF
Sample wt & glue (gm)	.0838	.0622	.0926	.0813	.0704	.0379	.0765	.0573
H_2O wt (gm)	.088	.0232	.0957	.0364	.0245	.0092	.0848	.08
Vol % H_2	62.2	51.8	59.3	46.1	47.42	45.0	57.7	59.4
CO	30.4	43.4	34.2	47.3	46.17	46.2	35.1	33.4
CO_2	6.6	3.1	5.6	1.3	1.2	1.3	5.3	5.5
CH_4	.9	1.0	.9	2.7	2.5	2.9	1.5	1.3
C_2H_4	0	.2	0	.5	.6	.7	.4	.4
C_2H_2	0	0	0	2.1	2.1	4.0	0	0

Note: All conditions unless specified are T_o = 25°C, P_o = 1 atm (N_2), V_c = 521 ml, 76mm wire sample, 4 mm ID glass tube surrounding sample.

A = tube sealed at ends using small corks.

TABLE 18

Experimental Results: Samples in a Hydrogen Atmosphere

Run Number	46	47	25[A,B]	48	49	38[A]	50	51	36[A]
ΔP cmH_2O	14.6	36.5	16.5	16.9	16.9	34.1	18	35.3	31.3
Sample	cell	cell	cell	BF	BF	BF	Lig	Lig	Lig
Sample wt + glue (gm)	.0692	.0757	.1054	.0610	.0545	.0429	.1135	.1074	.0582
Vol % CO	89.79	89.91	91.6	79.66	78.5	84.14	68.09	70.65	74.12
CO_2	1.24	1.44	1.8	3.13	3.76	2.34	3.30	2.05	2.25
CH_4	3.63	4.32	3.2	7.40	8.27	5.01	10.64	8.20	5.14
C_2H_4	1.15	1.26	0	2.84	2.56	1.50	3.06	2.45	1.61
C_2H_2	4.2	3.06	3.6	6.97	6.92	5.84	14.91	16.66	17.52

Note: All conditions unless specified are T_o = 25°C, P_o = 1 atm (H_2), V_c = 521 ml, 76mm wire samples, 4 mm ID glass tube surrounding sample. H_2 normalized out of gas composition presented.

A = nitrogen atmosphere, H_2 normalized out of gas composition presented.

B = cell volume V_c = 1459 ml

Lower pressure increases were observed for samples in hydrogen, but this can be attributed to the formation of water produced from residual oxygen in the cell.

7.3.5 Fast Pyrolysis of Samples Containing Glue Only

Glue samples were treated in the same manner as other samples except that only glue covered the wire. The results are presented in Table 19. Runs 5 and 6 give an indication of how much gas was formed from glue in a typical run, since the weight of glue was judged to be representative of the amount used in biomass samples. A larger mass of glue was used in runs 46 to 48 for an accurate gas analysis. The composition of the gases from glue samples is very similar to the mean cellulose gas composition. It was therfore concluded that the glue had a negligible effect on the overall gas composition from cellulose samples.

A molecular formula C(6) H(12.2) O(5.06) was calculated from the averaged gas composition in runs 46 to 48. The major constituent of the glue is known to be polyvinyl acetate(C(6) H(9) O(3)).

TABLE 19

Experimental Results: Glue[A] Samples in a Nitrogen Atmosphere

Run Number	5	6	46	47	48	Cellulose[B]
ΔP cm H_2O	3	2.8	17.7	17.8	18.3	mean gas composition vol % / S.D.
Mass of Glue (gm)	.0109	.0045	.0708	.06310	.0726	
Vol % of gases H_2	32.2	40.8	46.70	48.39	48.20	46.88 / 1.55
CO	61.0	59.2	43.96	45.97	45.56	49.29 / 1.72
CO_2	6.8	0	.7	.99	1.06	.911 / .145
CH_4	0	0	5.6	1.25	1.14	1.32 / .27
C_2H_4	0	0	0	0	0	.233 / .23
C_2H_2	0	0	3.08	3.41	4.05	1.37 / .35

Note: All conditions unless specified are T_o = 25°C, P_o = 1 atm (N_2), V_c = 521 ml, 76mm wire sample,4 mm ID glass tube surrounding sample.

A: Lepages glue, Lepages Glue Ltd.

B: Mean composition from Runs 15-17, 25, 27-31.

7.3.6 Bare Wire Samples in a Nitrogen Atmosphere

The mysterious pressure increase experienced when a bare wire was volatilized appears to be from the formation of carbon monoxide and carbon dioxide. This conclusion is evident from Table 20, although there is some inconsistency between different runs. The average pressure increase was 2.2 cm water. This would account for less than 8 % of the pressure increase for most biomass samples. It is hard to imagine where these gases came from unless they were adsorbed on or in the metal wire and released during the explosion.

7.4 Mass Balances

7.4.1 Overall Mass Balance

The overall mass balance was not very helpful, since any tars or water formed during pyrolysis were unaccounted for. Also the explosive nature of the discharge across the wire sample scattered the residue in the test cell, making full recovery of the residue difficult if not impossible.

Table 21 contains the results from runs where an overall mass balance was attempted. Runs 14 and 22 were the most successful, recovering more than ninety percent of the original sample weight. A slow pyrolysis sample, run no. 8, showed a very poor recovery efficiency. This is

TABLE 20

Gas Analyses from Bare Wire Samples in a Nitrogen Atmosphere

Run Number	4	49	50	51	52	53	54	55	56	57
P cm H_2O	1.0	.9	2	1.2	1.6	1.9	3.6	4.1	1.7	2.1
Cell Volume	521	1459	521	521	521	521	521	521	521	521
Vol % of gases H_2	0	0	0	0	0	0	60.3	59.5	75.9	0
CO	28.7	100	82.2	100	74.1	84.9	39.7	40.5	24.1	100
CO_2	71.3	0	17.8	0	25.9	0	0	0	0	0
CH_4	0	0	0	0		15.1	0	0	0	0

Note: All the conditions unless specified are T_o = 25°C, P_o = 1 atm (N_2), 76 mm bare wire samples

TABLE 21

Overall Mass Balance Results

Run Number	19	14	21	22	15	23	8
Sample, sample + glue wt. (gm)	cell .0466	cell .0512	cell .0940	cell .1055	cell .068	cell .0605	cell .0245
% weight as gas	12.38	7.89	5.3	9.33	18.34	16.1	39.18
% weight as solid residue	74.25	83.2	62.98	81.04	54.41	62.64	23.67
% weight of sample unaccounted	13.37	8.91	31.72	9.63	27.25	21.26	37.15
Slow or fast pyrolysis	Fast	Fast	Fast	Fast	Fast	Fast	Slow

due to the relatively large amounts of tars or condensable gases formed during pyrolysis which were deposited on the cell walls. In fast pyrolysis testing there was no visual evidence of tar formation.

The gas mass was computed using the ideal gas law, the cell volume and pressure and the gas composition for individual runs.

7.4.2 Carbon Balance In The Gas Phase

Figure 11 shows the percentage carbon converted to gas plotted against the carbon mass on the wire. At best, the carbon conversion approached 40 percent when the sample originally contained less than .01 grams of carbon.

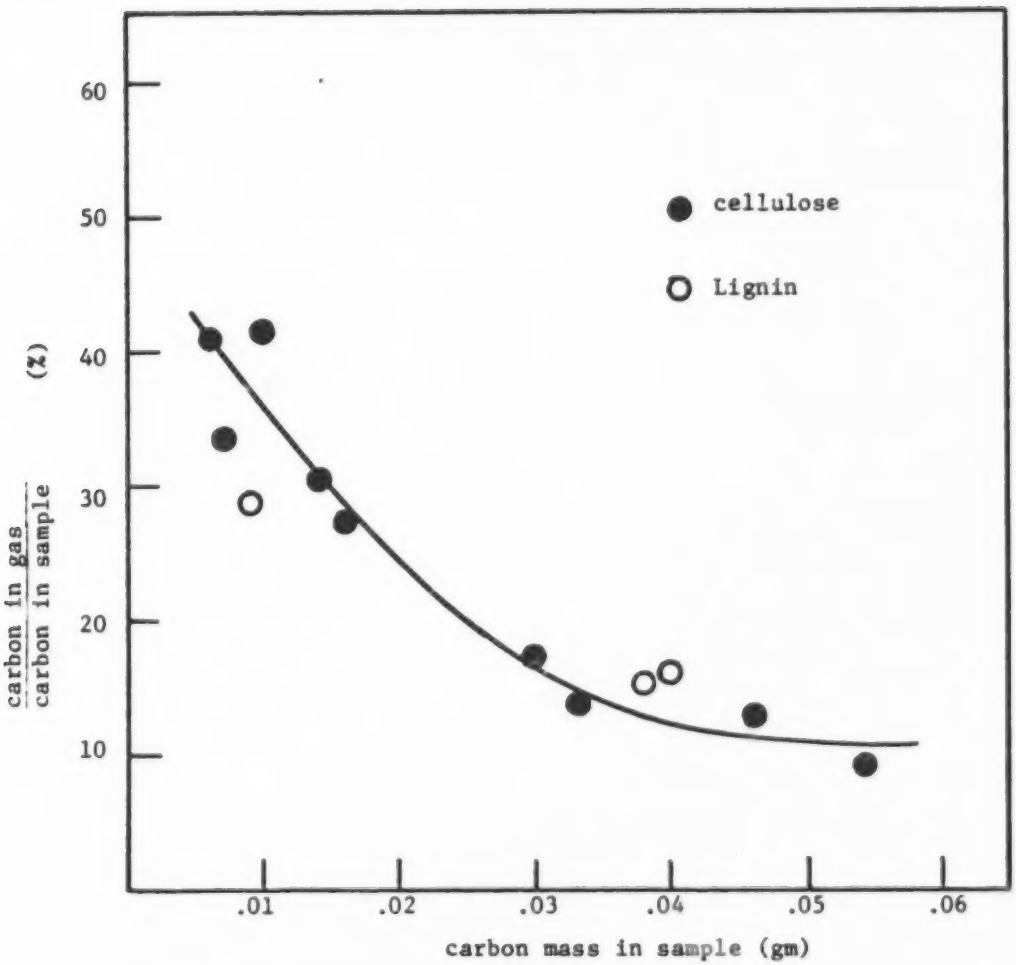


FIGURE 11: Carbon conversion to gas versus the amount of carbon on the wire

8 CONCLUSIONS

An experimental apparatus was constructed for studying electrical discharge flash pyrolysis. The apparatus consisted of a large capacitor, power supply and test cell, where the biomass was held between two electrodes. The capacitor was discharged across the electrodes, providing heat for pyrolysis of the biomass sample.

The novelty of the experimental apparatus was that discharges occurred in the range of 70-200 μsec. Pyrolysis of biomass occurring as a result of the capacitor discharge would be almost instantaneous, and the heating rate would be extraordinarily high.

Several sample types were studied. These included pelletzed samples, conductive string and cellulose coated wire samples.

Pelletized samples consisted of cellulose and graphite or activated carbon. Pressure readings and gravimetric measurements proved the material in the pellets was essentially unaffected by the capacitor discharge. It seems the pellets offered too high a resistance, so that the electrical pulse travelled through the cell atmosphere instead of through the sample. When the sample was

fractured during discharge, it appeared the current passed through the sample, however no measurable pyrolysis of the sample was observed.

Conductive string samples with a larger electrode separation failed to suppress conductance of the discharge through the inert atmosphere. Again the pressure increases and changes in sample weight were negligible, indicating poor interaction between the electrical discharge and the conductive string samples.

A thin wire placed between the electrodes was completely volatilized when the capacitor was discharged. By coating the wire in cellulose a fraction of the cellulose was pyrolyzed during discharge. This produced small amounts of pyrolysis gases in a nitrogen atmosphere. These gases, analyzed by gas chromatography, consisted mainly of hydrogen and carbon monoxide, with small amounts of hydrocarbons also present. The amount of sample gasified was of the order of 0.01 grams at the most.

Varying the nature of the biomass sample coating the wire and its moisture content produced some interesting changes in the gas composition. Lignin and birch flour samples yielded higher concentrations of acetylene, methane, and ethylene then cellulose samples. Moisture in all three biomass samples increased the concentration of

hydrogen in the gas.

Discharges across the wire-biomass samples in a hydrogen atmosphere showed no significant differences from discharges in a nitrogen atmosphere.

The experimental apparatus, using wire samples, was useful in producing and analyzing the gases from virtually instantaneous pyrolysis. However, it is difficult to calculate values for heating rate, maximum temperature obtained and closure of mass balances, due to the violent and rapid nature of the discharge. It was also difficult to measure any tar or water formation from pyrolysis because of the small sample weight.

Although some interesting results were recorded as regards gas composition from this fast method of pyrolysis, the experimental pitfalls previously mentioned discouraged any further work. Finally, it should be stated that in the opinion of the authors no commercial process for producing useful gases from biomass by electrical discharge suggests itself as the result of this study.

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POOR

QUALITY

ORIGINAL